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S. Taylor-Myers, J. G. Nuzzo, and J. F. Haw

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Two-dimensional ^{15}N MAS NMR spectrometry was used to characterize slow reorientation of the chromophore at temperatures well below T_g in the prototypical nonlinear optical (NLO) polymer 10% 4-nitroaniline- $^{15}\text{N}_2$ /poly(methyl methacrylate). Qualitative analysis of 2D contour plots obtained for various mixing times at 289 K suggests that significant reorientation takes place between 0 ms and 200-300 ms, and little or no further change occurs up to 2000 ms. Straightforward statistical arguments were used to devise a simple model for quantitative analysis of integrated peak intensities in 2D MAS spectra. This analysis demonstrates that the chromophore undergoes random isotropic reorientation at the longest mixing times used and permits a calculation of the fraction of oriented chromophore remaining at any intermediate mixing time. The data at 298 K are well fit by an exponential autocorrelation function with a time constant of 91 ms. Limited data obtained at 323 K demonstrate that the chromophore reorientation is thermally activated and permit a rough estimate of the activation energy.

The methods reported here should be readily applied to the characterization of chromophore dynamics at moderately long time scales for a variety of NLO polymer materials.

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Dr. James F. Haw

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Characterization of Slow Chromophore Reorientation in
Nonlinear Optical Polymers by Two-Dimensional MAS NMR

Sharon Taylor-Myers, James G. Nuzzo, and James F. Haw*

Department of Chemistry, Texas A&M University, College Station, Texas 77843

Abstract

Two-dimensional ^{15}N MAS NMR spectrometry was used to characterize slow reorientation of the chromophore at temperatures well below T_g in the prototypical nonlinear optical (NLO) polymer 10% 4-nitroaniline- $^{15}\text{N}_2$ /poly(methyl methacrylate). Qualitative analysis of 2D contour plots obtained for various mixing times at 289 K suggests that significant reorientation takes place between 0 ms and 200-300 ms, and little or no further change occurs up to 2000 ms. Straightforward statistical arguments were used to devise a simple model for quantitative analysis of integrated peak intensities in 2D MAS spectra. This analysis demonstrates that the chromophore undergoes random isotropic reorientation at the longest mixing times used and permits a calculation of the fraction of oriented chromophore remaining at any intermediate mixing time. The data at 298 K are well fit by an exponential autocorrelation function with a time constant of 91 ms. Limited data obtained at 323 K demonstrate that the chromophore reorientation is thermally activated and permit a rough estimate of the activation energy.

The methods reported here should be readily applied to the characterization of chromophore dynamics at moderately long time scales for a variety of NLO polymer materials.

*Author to whom correspondence should be addressed

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Introduction

Much current interest is focussed on materials with nonlinear optical (NLO) properties, especially NLO polymers.¹ These materials are prepared by incorporating a chromophore into a glassy or liquid crystalline polymer by one of several methods.²⁻⁶ The chromophore may be dissolved or doped into the host polymer and then be covalently attached to it by either radiative or chemical crosslinking. Alternatively, the chromophore may be incorporated into the polymer by direct synthesis either in the main chain or as a pendant group. The most common application of NLO polymers, second harmonic generation, requires a macroscopic orientation of the chromophores. This is typically achieved by poling the material in an intense electric field at a temperature above the glass transition or before completing the polymerization or crosslinking process. The macroscopic orientation thus established is preserved by chemical reaction and/or cooling below T_g before removal of the poling field.

A major problem with NLO polymers relative to competitive crystalline materials is loss of second harmonic properties due to reorientation of the chromophores. For poled materials, the loss of macroscopic orientation can most easily be followed by direct measurement of the decay of second harmonic intensity over time. It is desirable to apply physical characterization methods for chromophore motion that do not require macroscopic orientation, as such methods can allow an evaluation of different synthetic strategies for chromophore immobilization before attempting to prepare poled films. In a recent communication,⁷ we described the use of one-dimensional ^{15}N MAS NMR to study the dynamics of 4-nitroaniline- $^{15}\text{N}_2$. In that study, the random orientation of the chromophore in the unpoled material was reflected in the sideband pattern due to the chemical shift anisotropy (CSA) of the nitro group. Motion of the

chromophore molecules on a time scale approaching the sample rotation period was reflected in a progressive broadening and coalescence of the sideband pattern as the temperature was raised to T_g . Application of the theory of Waugh and coworkers⁸ permitted us to estimate that the 4-nitroaniline chromophore was tumbling isotropically on a time scale of 0.06 ms at a temperature of ca. 10 K below T_g .

In practice, NLO polymers are used at temperatures well below T_g , and one is concerned with measuring loss of orientation on significantly longer time scales. In the present contribution, we describe the application of a 2D ^{15}N experiment originally developed by Veeman and coworkers⁹ to 4-nitroaniline- $^{15}\text{N}_2$ in PMMA at temperatures well below T_g . This method is capable of detecting reorientation on time scales on the order of T_1 , which can be tens or hundreds of seconds for ^{15}N in rigid solids. Using this method, we have measured the autocorrelation function for the reorientation of the chromophore. At 298 K, this function was well described by an exponential with a time constant of 91 ms. Comparison of this result with a single measurement at 323 K suggests an activation energy for rotational diffusion on the order of 37 kJ/mol.

Experimental Section

Materials. 4-Nitroaniline- $^{15}\text{N}_2$ (95% enriched) was obtained from Cambridge Isotope Laboratories. Poly(methyl methacrylate), PMMA, and poly(vinyl cinnamate), PVCN, were obtained from Aldrich. Doped NLO polymer samples were prepared by dissolving the polymer and enough chromophore for a 10% loading in either chloroform (PMMA) or toluene (PVCN). After mild stirring, the solutions were transferred to glass plates and dried slowly to remove solvent. The resulting films were optically clear and showed no evidence of phase separation.

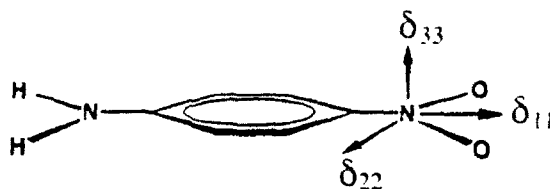
All polymer samples were characterized by differential scanning calorimetry on a Mettler DSC 30 at Dow Chemical Co. in Freeport, TX. Samples were heated to 448 K and then cooled under nitrogen to establish a uniform history before measuring the glass transition on a second ramp at a heating rate of 20 K min⁻¹. The undoped polymers had T_g s of 390 K (PMMA) and 357 K (PVCN). After doping, these values were reduced to 357 K and 336 K, respectively. All of the results reported here were obtained for the PMMA host polymer, but the PVCN system showed qualitatively similar behavior.

Spectroscopy. All NMR experiments were performed on a Chemagnetics CMX-360 operating at 36.5 MHz for ¹⁵N. One-dimensional spectra were acquired with cross polarization below T_g and direct excitation (Bloch decay) above T_g . Two-dimensional exchange spectra of spinning samples were acquired at temperatures below T_g using the pulse program in Figure 1. The cross polarization contact time was 5 ms and the pulse delay was 1 s. As discussed by Veeman and coworkers,⁹ the mixing time τ must be an integer multiple of the rotor period in order to avoid spurious cross peaks due to macroscopic reorientation of the sample. Spinning speeds were stabilized using a Chemagnetics spin-speed controller and were 2000 ± 1 Hz for all 2D experiments. The phase cycling scheme used for the experiment in Figure 1 does not preserve quadrature information, so the transmitter was set to one side of the spectrum, and the 2D data sets were processed to yield magnitude spectra. 128 t_1 increments between 0 and 2.54 ms were used, and a 256-point FID was acquired in each case by signal averaging 200 scans. The data sets were zero-filled to 256 X 256 and apodized with a sine-bell window before transformation. Data processing was performed using Felix (Hare Associates).

Results and Discussion

Figure 2a shows a nonspinning ^{15}N cross polarization spectrum of a pure polycrystalline sample of 4-nitroaniline- $^{15}\text{N}_2$. This spectrum shows resolved powder patterns due to the NO_2 resonance, which has a large CSA, and a narrower pattern due to the NH_2 resonance. As shown in Figure 2b, slow speed MAS preserves information about the distribution of orientations of the NO_2 group in the spinning sideband pattern. Spinning provides a major advantage in sensitivity; Figure 2b required 8 scans vs. 800 for the nonspinning spectrum in 2a. Figure 2c shows a spectrum of 10% 4-nitroaniline in PMMA at 173 K that was obtained at a near-identical spinning speed to that of the pure chromophore in 2b. Motion of the dissolved chromophore is negligible on the ms time scale at this temperature, and the CSA of the NO_2 group for the dissolved molecule is nearly identical to that in the crystalline state.

The principal components of the $^{15}\text{NO}_2$ chemical shift tensor were determined from Figure 1a by inspection, and were found to be $\delta_{11} = 91$ ppm, $\delta_{22} = 41$ ppm, and $\delta_{33} = -200$ ppm. (Note that these values were reported incorrectly in reference 7). The orientation of the chemical shift tensor was assigned by analogy to nitrobenzene.



As shown in Figure 3, at temperatures 30 K or more below T_g , motion of the chromophore is slow enough that the CSA is not averaged, and distinct sideband patterns are observed. At approximately 10 K below T_g (e.g., 348 K, Figure 3), the timescale of molecular tumbling of the chromophore becomes comparable to the MAS rotor period, or more specifically

$(\sqrt{2}\omega_r)^{-1}$, and coalescence of the sideband pattern occurs. In reference 7, the chromophore was assumed to tumble isotropically 10 K below T_g , and the theory developed by Waugh and coworkers⁸ was used to calculate a correlation time of 0.06 ms at that temperature. NLO polymers are designed to be operated at temperatures well below the onset of rapid motion, and it is desirable to have methods to measure chromophore reorientation on much longer time scales.

Appropriate 2D or 3D exchange experiments are frequently applied to characterize slow exchange phenomena in condensed phases. Spiess has recently reviewed the application of such methods to the measurement of orientation and dynamics of solid polymers.¹⁰ Multidimensional exchange experiments probe dynamics at long time scales limited only by the T_1 of the nucleus studied. For 10% 4-nitroaniline- $^{15}\text{N}_2$ in PMMA at 298 K, the ^{15}N T_1 values were 49 s for the NO_2 resonance and 5 s for the NH_2 signal. In general, T_1 values become longer with decreases in mobility (induced by, for example, crosslinking), and ^{15}N T_1 s for nonprotonated nitrogens in rigid solids on the order of many minutes are not uncommon.

The most straightforward 2D ^{15}N experiment for studying reorientation of 4-nitroaniline in PMMA would be a nonspinning experiment. Analogous ^2H and ^{13}C studies have been applied in investigations of polymer backbone motion.¹⁰ Such experiments can readily distinguish between isotropic rotational diffusion and various types of jumping motions based on the appearance of the off-diagonal intensity. A nonspinning 2D ^{15}N exchange experiment was attempted for the 10% 4-nitroaniline- $^{15}\text{N}_2$ /PMMA system, but the signal to noise attainable in a reasonable acquisition time was not sufficient to elucidate the details of the motion. We therefore took advantage of the increased sensitivity available by slow speed MAS. This

experiment can either be done in the manner originally described by Veeman,⁹ or by the method described by Hagemeyer et al. that uses four data sets to generate better resolved absorptive spectra.¹¹ The original experiment gave satisfactory results and was used for all of the results reported here.

A number of 2D ^{15}N experiments were obtained for the PMMA system at 298 K with mixing times ranging from 0 to 2000 ms. A smaller number of studies were performed at 323 K to unambiguously establish that the magnetization transfer process was thermally activated and to provide an estimate of the activation energy for chromophore reorientation. In order to facilitate comparison with the one-dimensional variable temperature spectra in Figure 3, all 2D experiments were performed with a spinning speed of 2000 Hz. Figures 4 through 6 report 2D ^{15}N exchange spectra at 298 K. Since only the $^{15}\text{NO}_2$ resonance shows appreciable sideband intensity, the 2D spectra are presented in a manner that emphasizes this region and excludes the $^{15}\text{NH}_2$ region. Figure 4a shows the spectrum obtained with a 0-ms mixing time. This spectrum shows resonances along the main diagonal corresponding to the isotropic peak and the two orders of sidebands with appreciable intensity. The relative integrated intensities of these peaks are consistent with the intensities of the corresponding one-dimensional spectra. Small cross peaks were observed with a 50-ms mixing time (Figure 4b). Further increases in mixing time (Figures 5 and 6) result in progressive increases in sideband intensity up to a mixing time of 200 ms, and a small further increase at 300 ms, but no further increase at 2000 ms.

The two general mechanisms for magnetic exchange are spin diffusion¹² and chemical site exchange, the latter corresponds to changes in molecular orientation in the present case. Spin diffusion relies on energy-conserving spin flips, and would not be efficient in the present case.

The temperature dependence of the exchange rate (vide infra) and the absence of cross peaks connecting the $^{15}\text{NO}_2$ and $^{15}\text{NH}_2$ resonances in any experiment strongly rule out spin diffusion as a contribution to the magnetization transfer process observed in these experiments.

Veeman and coworkers have developed the formalism necessary to simulate peak intensities in 2D spinning experiments for arbitrary choices of molecular reorientation;^{9,13} however, a complex formal analysis of the data reported here is not necessary in order to measure the autocorrelation function describing loss of chromophore orientation over time. The starting point in this analysis is to recognize that the relative integrated intensities of the theoretical 2D spectrum in the limit of completely random isotropic reorientation is directly calculable from the experimental spectrum with a zero mixing time. Each 2D spectrum can be thought of as a 5 X 5 matrix of integrated intensities. In the absence of exchange (Figure 4a), the off-diagonal components are zero. Each diagonal peak can be thought of as reflecting a set of orientations of the chromophore, and the relative intensities reflect the probability weighting of each set. Neglecting relaxation, the total integrated intensity of the matrix in the limit of complete isotropic reorientation will be identical to that before reorientation, but the intensity values will be redistributed. Since the probability of finding the chromophore at a particular orientation at one time and a second orientation at a later time is the product of the individual probabilities for the case of random reorientation, a similar rule applies to the relative intensities in the 2D spectrum at very long mixing times. For example, the intensity of any diagonal peak in the limit of complete reorientation should be the square of the intensity of that peak at zero mixing time, while the off-diagonal peak intensities should be predicted by the product of the corresponding diagonal peaks at zero mixing time. This procedure was used to calculate the

integrated intensities of each peak in the theoretical spectrum in the limit of isotropic reorientation, and these intensities were in excellent agreement with those measured from the experimental spectrum obtained with a 2000-ms mixing time. One can get a feel for this agreement from Figure 7. The experimental 2D data set in Figure 4a was subjected to a point-by-point multiplication process similar to that described above to generate a theoretical contour plot in the limit of complete exchange that is shown in Figure 7a. Aside from some line shape distortions reflecting digital resolution, the theoretical contour plot is in very good agreement with the experimental 2D data set obtained with a 2000-ms mixing time (repeated in Figure 7b for comparison). This agreement demonstrates that the chromophore completely and isotropically reorients in 2000 ms or less at 298 K. Furthermore, this is a reasonable result given the clear evidence of large amplitude reorientation on much shorter time scales implied by the presence of large cross peaks at much shorter mixing times.

In order to analyze the 2D spectra at intermediate mixing times, we considered the following model. We assumed that at any intermediate mixing time there was a fraction (f) of the chromophores that had not reoriented, whereas the remainder ($1-f$) had undergone large amplitude, isotropic reorientation. This model is physically plausible in terms of free volume arguments. Motion well below T_g can be driven by infrequent fluctuations in the polymer lattice which momentarily permit relatively unrestricted tumbling of small dissolved molecules. Each 2D spectrum in Figures 4-6 was used to calculate a matrix of integrated intensities at various mixing times, and each of these was modeled as a weighted sum of the zero mixing time matrix and the theoretical matrix in the limit of complete reorientation. In every case, the fraction, f , of oriented chromophores was determined by finding the weighting factor which minimized the

sum of the squares of the residuals between the experimental and simulated intensity matrices. Satisfactory fits were obtained in every case. The plot of f as a function of time, which is shown in Figure 8, is effectively the autocorrelation function for reorientation of the 4-nitroaniline chromophore. These data were fit very well by a simple exponential correlation function with a time constant of 91 ms.

Figure 9 reports 2D contour plots measured at 323 K for the same 10% 4-nitroaniline- $^{15}\text{N}_2$ /PMMA system. Qualitative inspection of these data suggests that reorientation of the chromophore in 50 ms occurs to a significantly greater extent at 323 K compared to 298 K, consistent with a thermally activated process. The data in Figure 9 were analyzed as before, and a reorientational correlation time of 29 ms at 323 K was estimated. The two correlation times were used to make a very rough estimate of the activation energy for chromophore reorientation, which was found to be on the order of 37 kJ/mol at temperatures well below T_g .

The procedures described here should be applicable to the study of other types of NLO polymers. For more complex chromophores such as those based on azo dyes, the determination of autocorrelation times for reorientation of individual nuclear sites should be possible.

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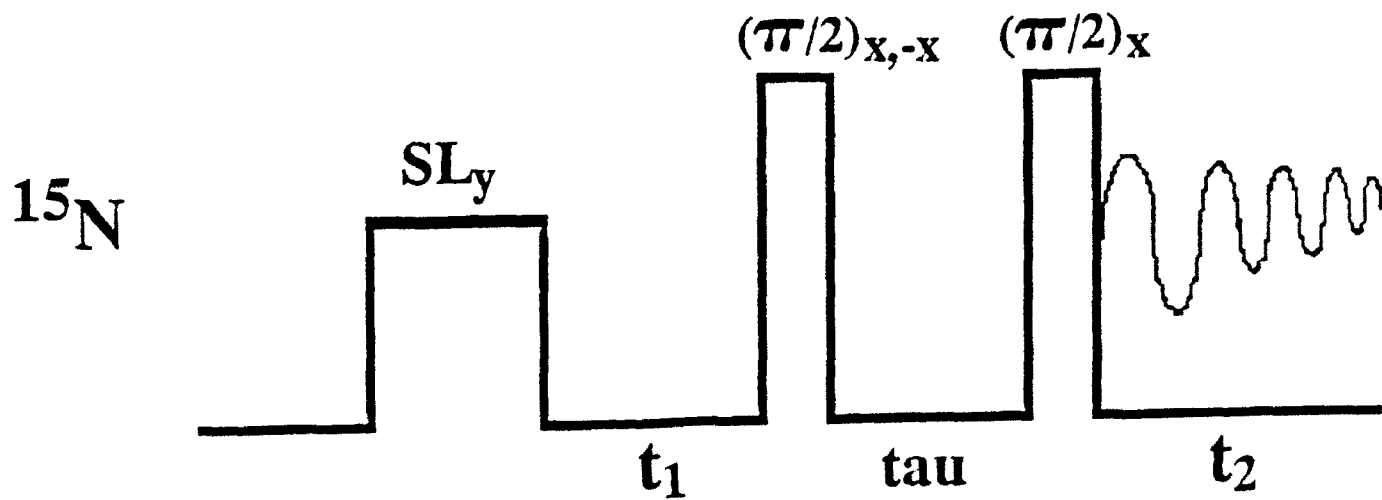
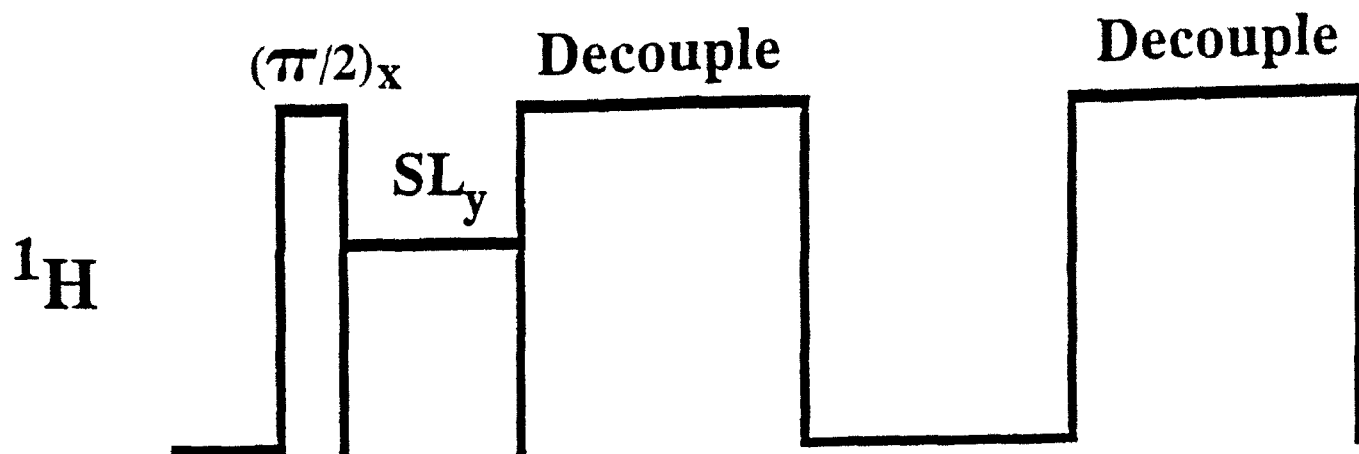
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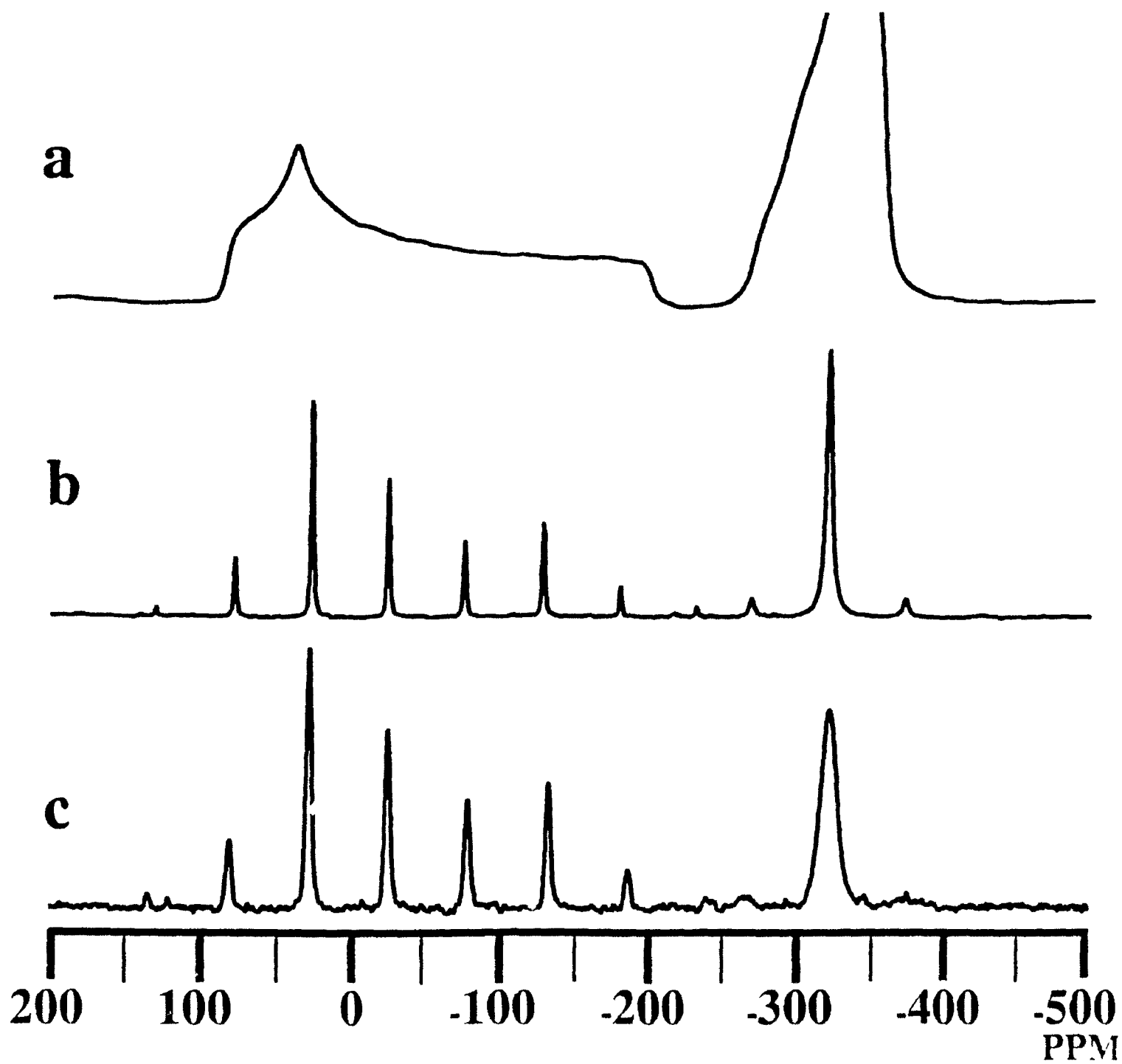
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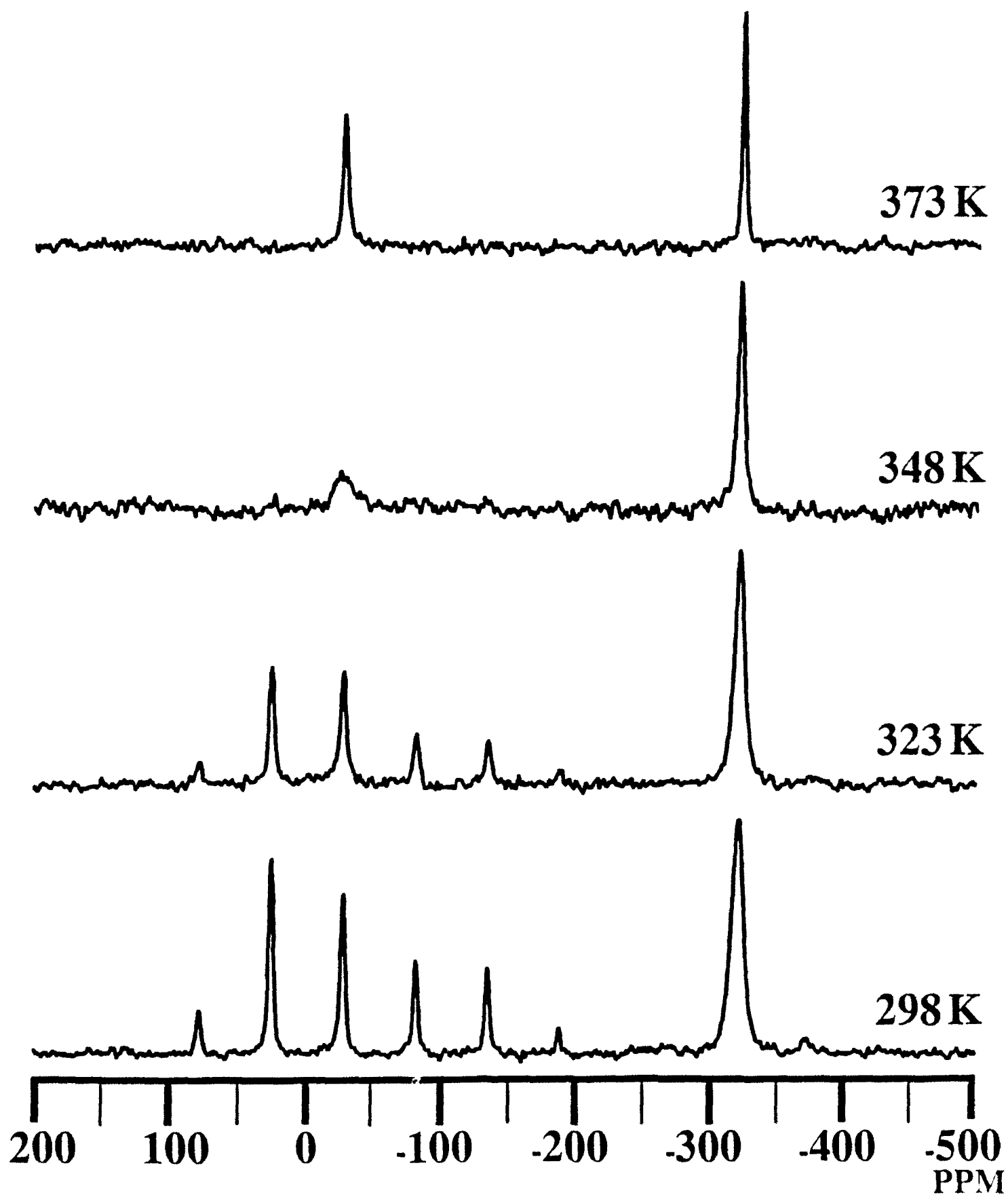
Figure Captions

- Figure 1. Pulse sequence used to acquire the 2D spectra reported in this contribution. The mixing period (τ) must be set to an integer multiple of the rotor period to avoid artifacts.
- Figure 2. ^{15}N spectra of 4-nitroaniline- $^{15}\text{N}_2$: (a) nonspinning cross polarization spectrum of the pure polycrystalline solid, 800 scans; (b) CPMAS spectrum of the pure solid at 298 K, 8 scans; (c) CPMAS spectrum of 10% 4-nitroaniline- $^{15}\text{N}_2$ in PMMA at 173 K, 300 scans.
- Figure 3. One-dimensional variable temperature ^{15}N MAS spectra of 10% 4-nitroaniline- $^{15}\text{N}_2$ in PMMA. Large amplitude motion of the chromophore on the time scale of the MAS rotor period leads to coalescence of the sideband patterns at ca. 10 K below T_g . All spectra were acquired with a spinning speed of 2000 Hz.
- Figure 4. 2D ^{15}N exchange spectra of 10% 4-nitroaniline- $^{15}\text{N}_2$ in PMMA at 298 K measured using mixing times of: (a) 0 ms; (b) 50 ms.
- Figure 5. 2D ^{15}N exchange spectra of 10% 4-nitroaniline- $^{15}\text{N}_2$ in PMMA at 298 K measured using mixing times of: (a) 100 ms; (b) 150 ms.
- Figure 6. 2D ^{15}N exchange spectra of 10% 4-nitroaniline- $^{15}\text{N}_2$ in PMMA at 298 K measured using mixing times of: (a) 300 ms; (b) 2000 ms.
- Figure 7. 2D ^{15}N exchange spectra of 10% 4-nitroaniline- $^{15}\text{N}_2$ in PMMA at 298 K in the limit of complete reorientation: (a) transition spectrum calculated from the 0-ms experimental spectrum using the procedure described in the text; (b) experimental result obtained with a 2000-ms mixing time.

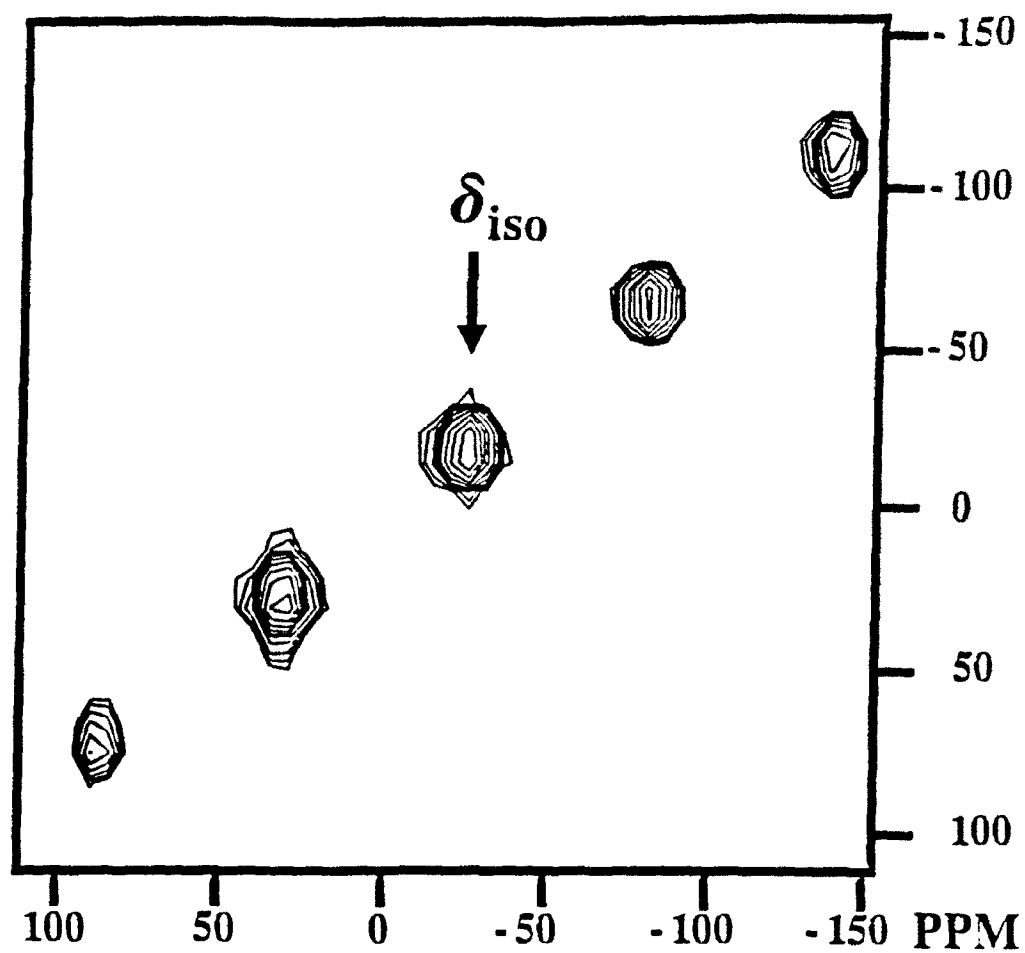
- Figure 8. Autocorrelation function for the decay in the fraction (f) of oriented chromophore molecules over time at 298 K. Data points were calculated from the experimental 2D spectra in Figures 4-6 using the procedure described in the text. The solid line is the best fit to a simple exponential yielding a time constant of 91 ms.
- Figure 9. 2D ^{15}N exchange spectra of 10% 4-nitroaniline- $^{15}\text{N}_2$ in PMMA at 323 K measured using mixing times of: (a) 0 ms; (b) 50 ms.



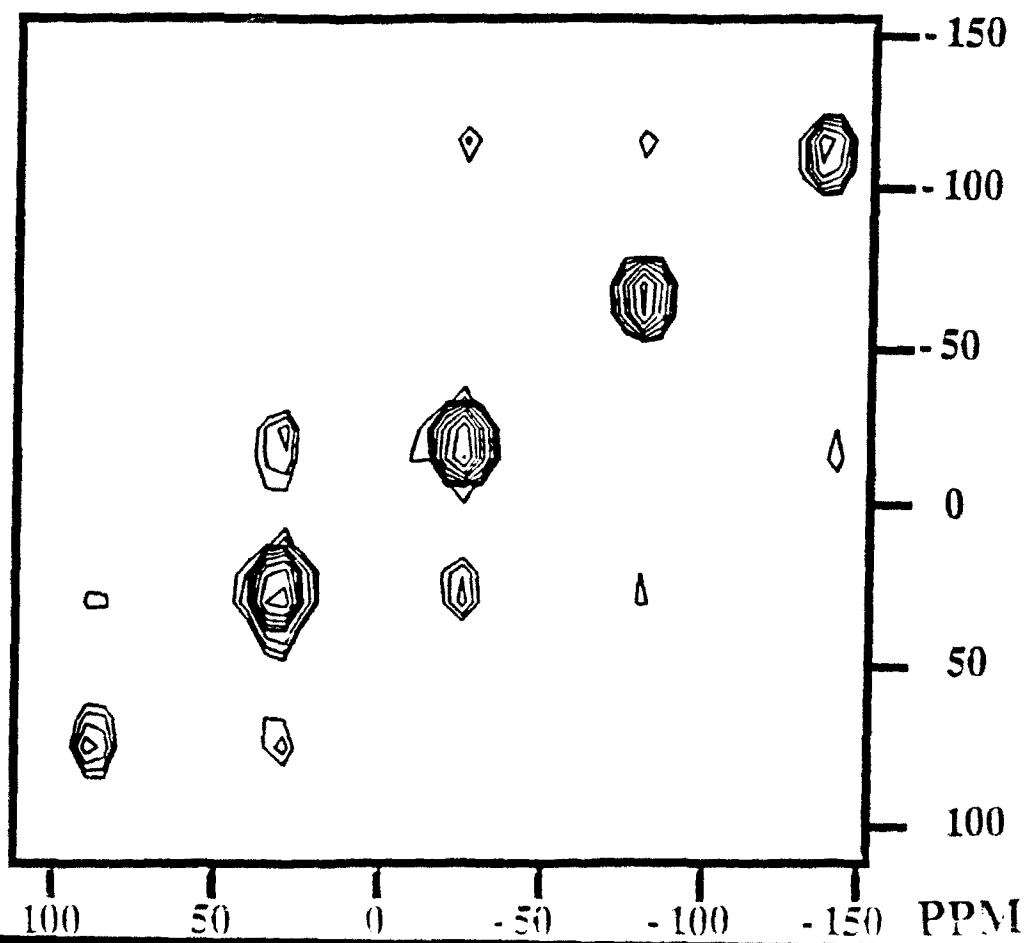




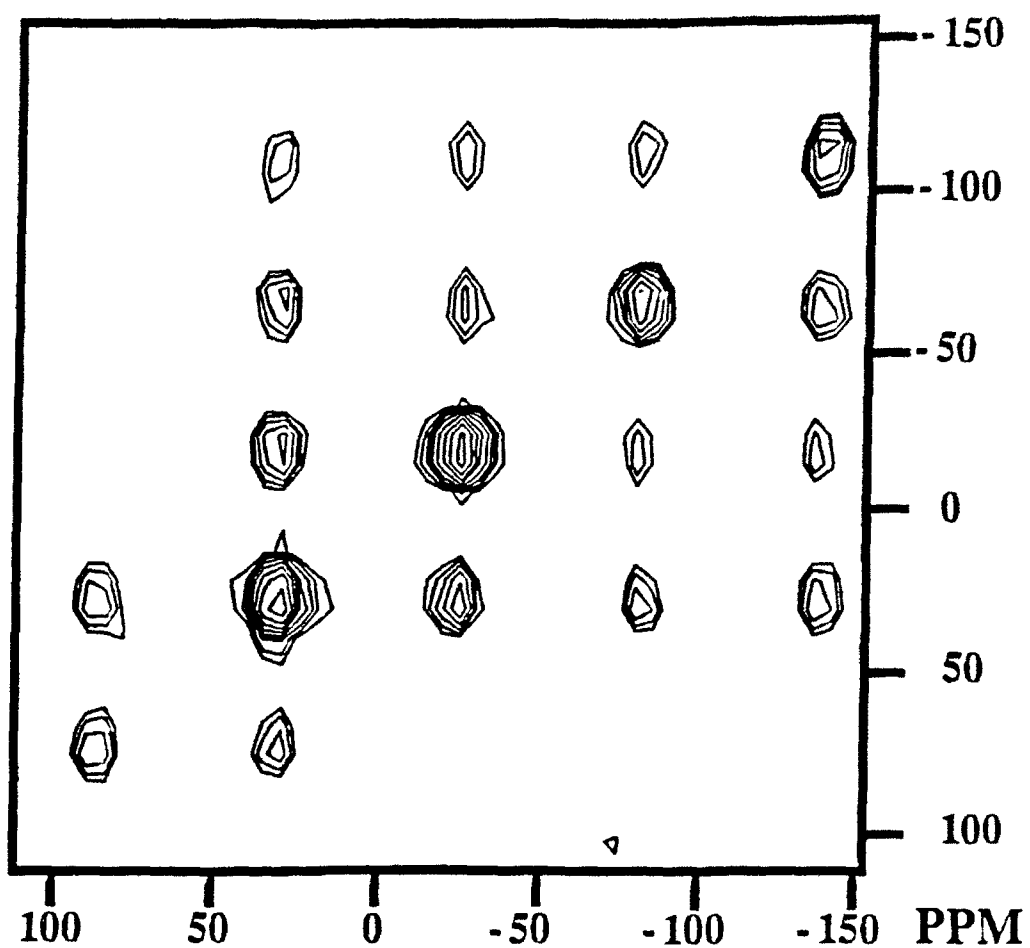
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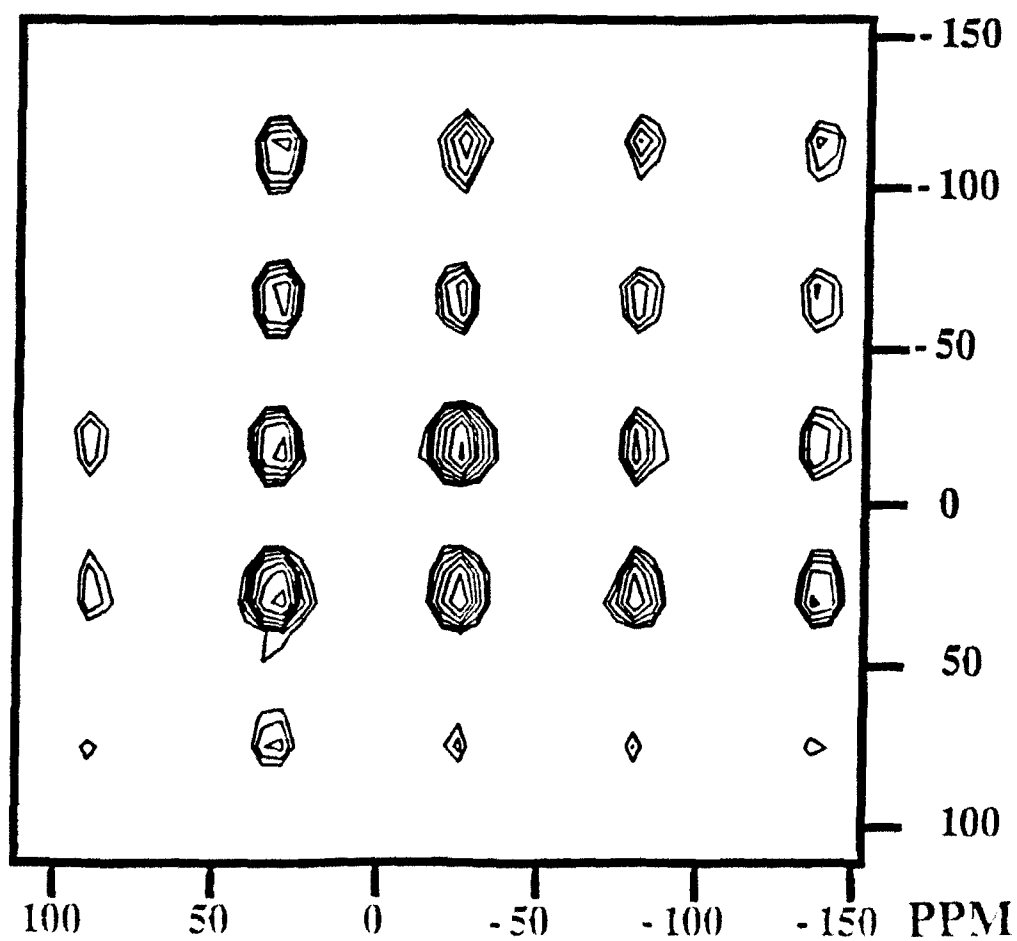
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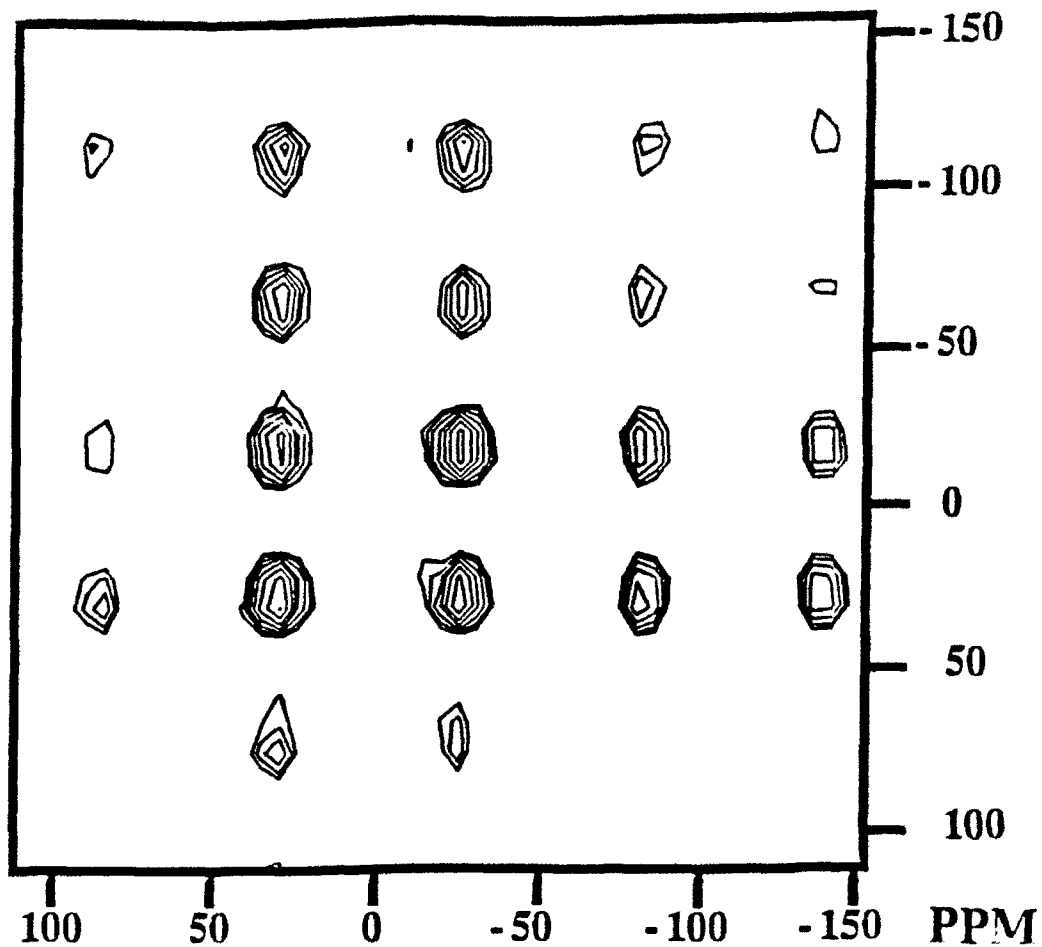
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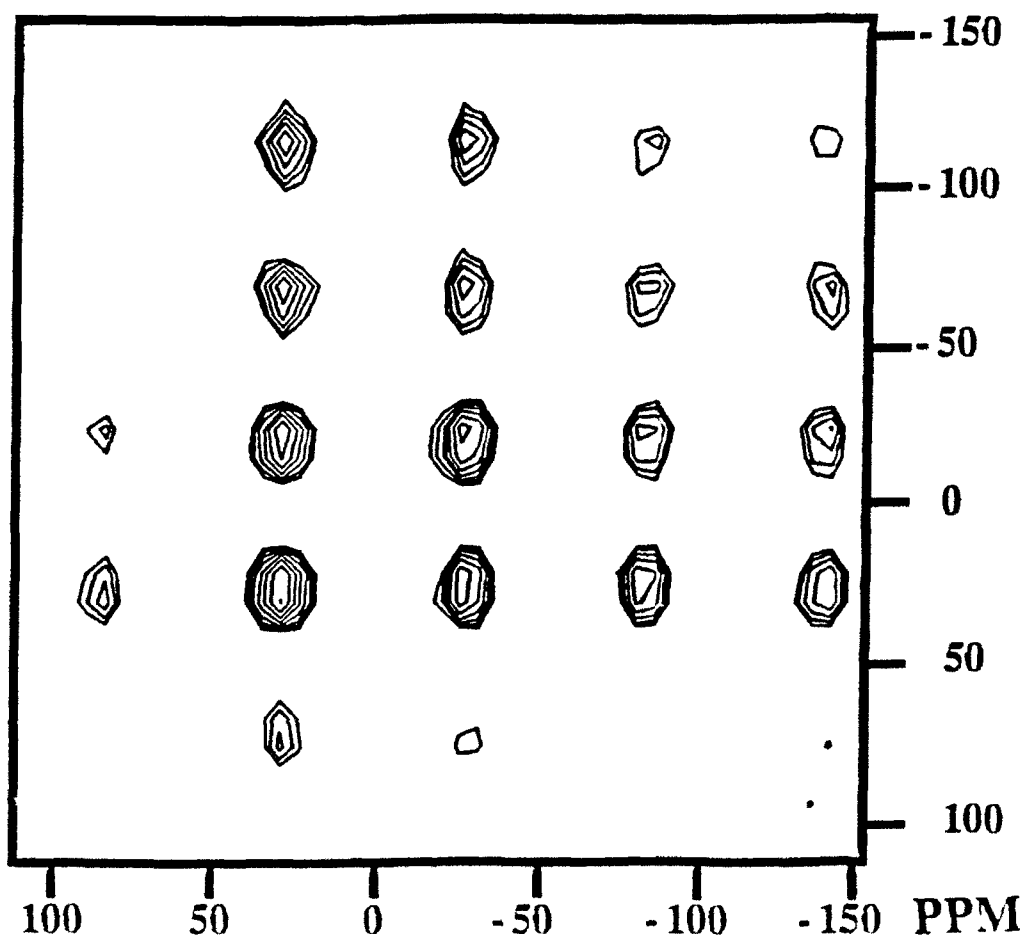
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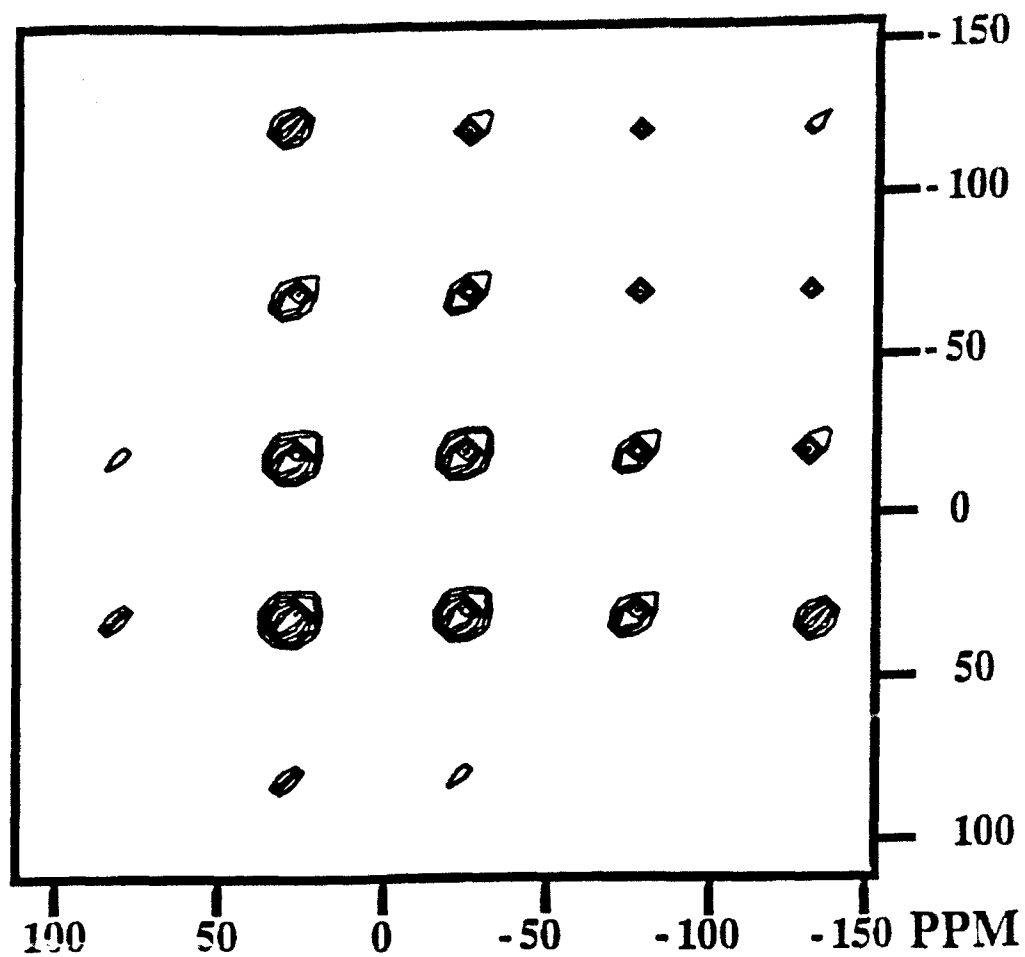
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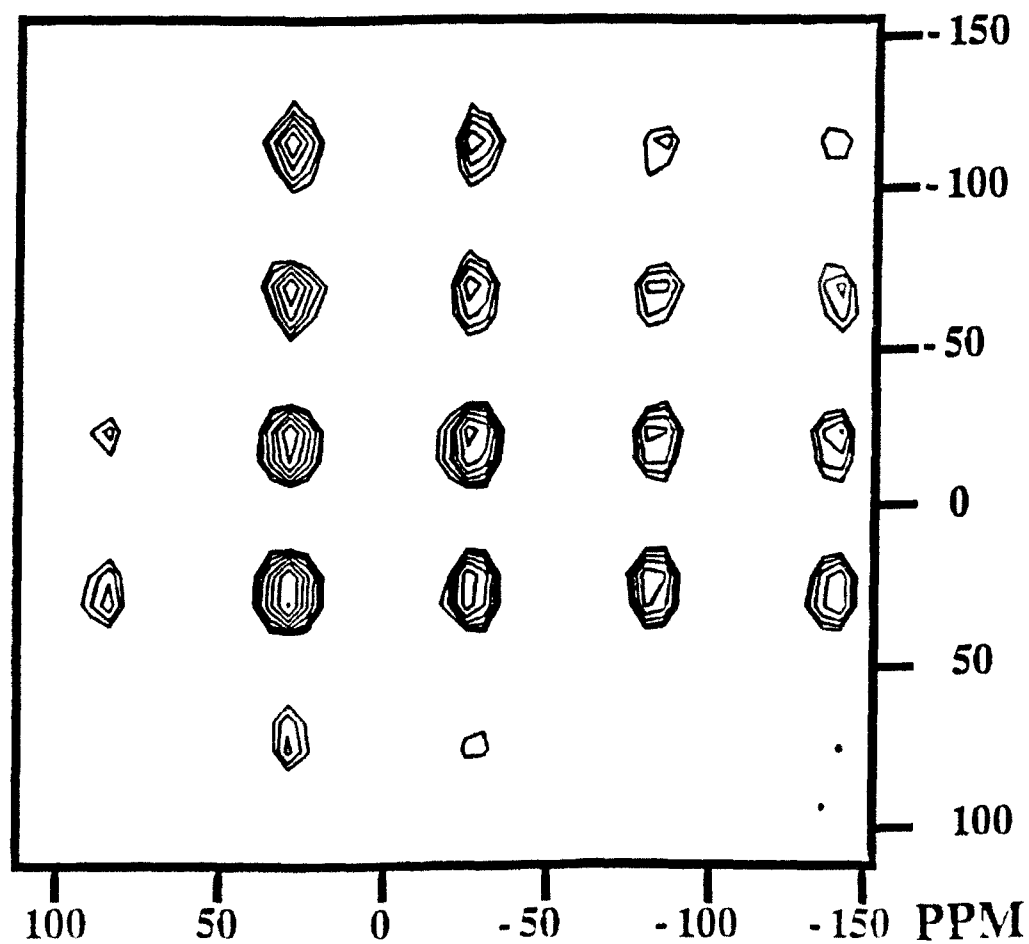
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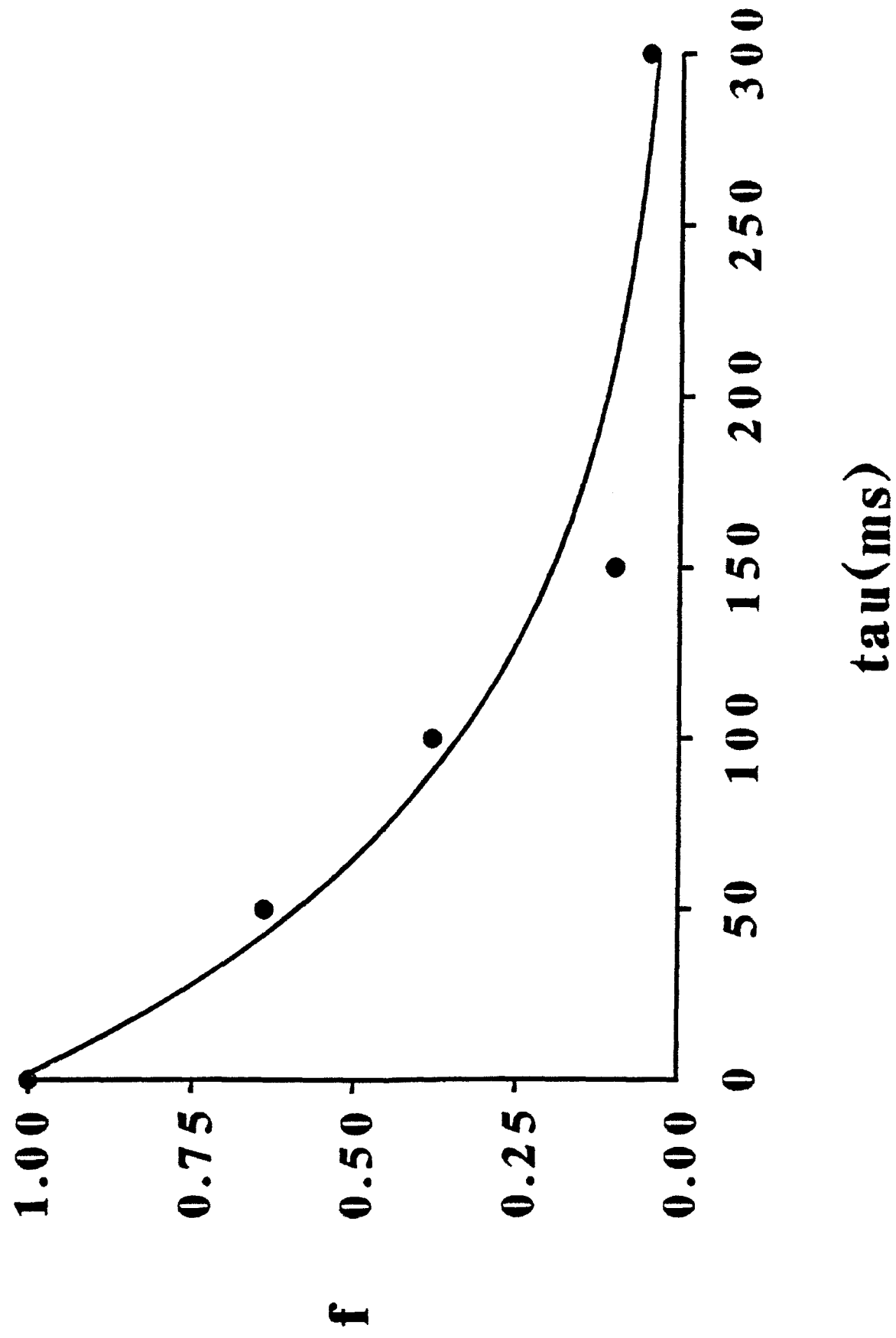


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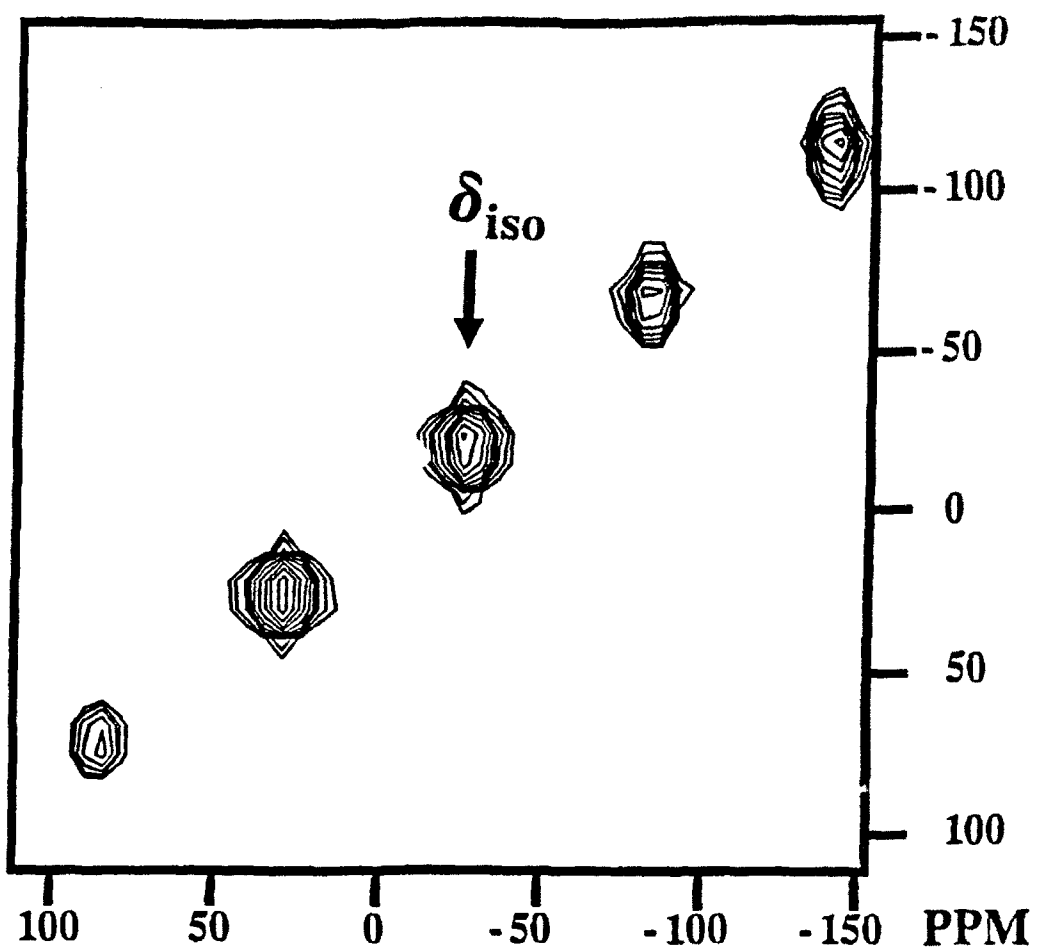


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